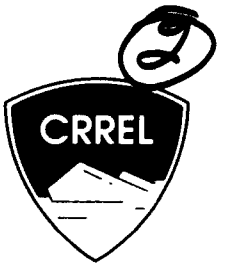

SPECIAL REPORT 92-25

Comparison of Cartridge and Membrane Solid-Phase Extraction With Salting-Out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives from Water

Thomas F. Jenkins, Paul H. Miyares, Karen F. Myers,
Erika F. McCormick and Ann B. Strong

December 1992

Abstract

Salting-out solvent extraction (SOE) was compared with cartridge and membrane solid phase extraction (SPE) for preconcentration of nitroaromatic and nitramine explosives from water, prior to reversed-phase high performance liquid chromatographic analysis (RP-HPLC). The procedures were compared initially using reagent grade water fortified with TNT, RDX, HMX and nine other analytes at concentrations below what could be determined without preconcentration and the results were used to estimate analyte recovery and the low concentration detection capability, as characterized by the Certified Reporting Limit (CRL). CRLs for the three procedures were comparable with values generally in the range of 0.05 to 0.30 μg/L. Percentage recoveries for the three procedures were generally greater than 90%, except for those of HMX and RDX obtained by the membrane-SPE procedure. A second comparison among the three procedures was obtained on 58 groundwater samples from the Rockeye site at the Naval Surface Warfare Center, Crane, Indiana. Results from a direct analysis procedure were compared to those from the three preconcentration techniques to estimate percent recovery of HMX, RDX and TNT for real samples. Recoveries were greater than 80% except for HMX and RDX by the membrane-SPE method. Both SPE procedures exhibited background interferences, which the authors attribute to matrix interaction with the SPE polymers. Usability of the three procedures in a production-oriented laboratory was evaluated with emphasis on solvent consumption, waste production and sample processing time. The cartridge-SPE was judged to be the least rugged of the three procedures.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, *Metric Practice Guide*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Special Report 92-25

US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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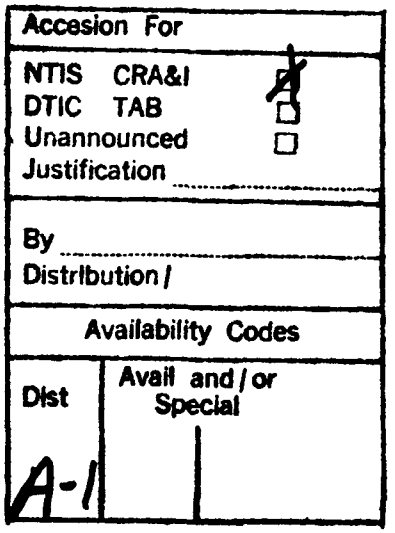

Prepared for
U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
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and
U.S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION

PREFACE

This report was prepared by Dr. Thomas F. Jenkins and Paul H. Miyares, Research Chemists, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and by Karen F. Myers, Research Biologist, and Erika F. McCormick and Ann B. Strong, Research Chemists, Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station (WES). Funding for this research was provided jointly by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (R-90, Multi-Analytical Services), Martin H. Stutz, Project Monitor, and the U.S. Army Waterways Experiment Station, Vicksburg, Mississippi (AF 25) Ann B. Strong, Project Monitor.

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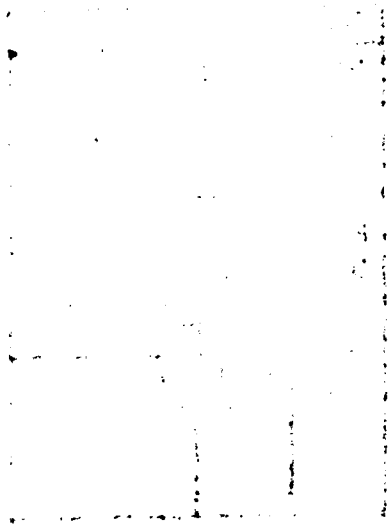

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Comparison of Cartridge and Membrane Solid-Phase Extraction With Salting-Out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives from Water

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ERIKA F. MCCORMICK AND ANN B. STRONG

INTRODUCTION

Classically, batch liquid-liquid extraction (LLE) has been used to extract trace organic analytes from water prior to analytical determination. The success of this approach depends upon favorable solvent/water partition coefficients (K_p) for the analytes of interest. Since many organic pollutants of environmental concern are relatively nonpolar, batch extraction with an immiscible organic solvent has been successful.

TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) (Fig. 1), along with several of their manufacturing impurities and environmental degradation products, have been observed in groundwater at a number of Army installations (Pugh 1982, Rosenblatt 1986, Spaulding and Fulton 1988, Maskarinec et al. 1986, Layton et al. 1987). Health Advisories have been issued by the EPA for many of these compounds (Table 1), with drinking water criteria at sub-part-per-billion concentrations. For this reason, there has been a great deal of interest by the Army in developing analytical methods to enable determination of these compounds at trace levels in water. To detect these compounds at the sub-part-per-billion concentration, the first step in these methods has been preconcentration of the analytes using an extraction process.

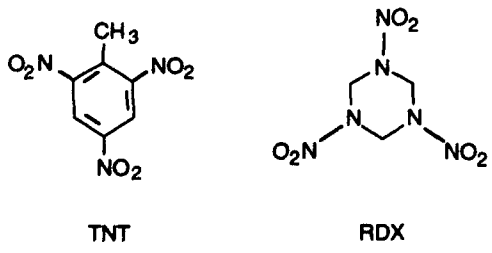

Figure 1. Chemical structures of TNT and RDX.

Classical LLE of these analytes has been reported. For example, Spanggord et al. (1982) reported extraction of TNT and many of its manufacturing impurities from water using diethyl ether. Phillips et al. (1983) used methylene chloride to extract nitroaromatics from biosludge. Belkin et al. (1985) developed a simple method for extracting nitroaromatics from water using toluene. Belkin reported, however, that poor extraction efficiency

Table 1. Proposed drinking water criteria for nitroaromatics and nitramines.

Compound	*Proposed drinking water limit (μg/L)*	*Reference*
HMX	400*	EPA 1988a
RDX	2.0*	EPA 1988b
TNT	2.0*	EPA 1989
2,4-DNT	50**	EPA 1992
	0.1	Etnier 1987
2,6-DNT	40**	EPA 1992
	0.007	Etnier 1987
1,3-DNB	1.0*	EPA 1991

* EPA Lifetime Health Advisory Number
** EPA number for increased cancer risk of 1.0×10^{-6}.

Table 2. Octanol/water partition coefficients (K_{ow}) for nitroaromatics and nitramines.

Compound	K_{ow}	*Reference*
HMX	1.15	Jenkins, 1989
RDX	7.31	Jenkins, 1989
2,4,6-trinitrobenzaldehyde	14.4	Jenkins, 1989
1,3,5-trinitrobenzene	15.1	Hansch and Leo, 1979
1,3-dinitrobenzene	30.9	Hansch and Leo, 1979
Tetryl	44.6	Jenkins, 1989
Nitrobenzene	70.8	Hansch and Leo, 1979
2,4,6-trinitrotoluene	72.0	Jenkins, 1989
4-amino-2,6-dinitrotoluene	81.5	Jenkins, 1989
2-amino-4,6-dinitrotoluene	87.2	Jenkins, 1989
2,4-dinitrotoluene	95.5	Hansch and Leo, 1979
2,6-dinitrotoluene	104	Jenkins, 1989
Benzene	135	Hansch and Leo, 1979
o-nitrotoluene	200	Hansch and Leo, 1979
p-nitrotoluene	234	Hansch and Leo, 1979
m-nitrotoluene	282	Hansch and Leo, 1979
Toluene	490	Hansch and Leo, 1979

Table 3. Methylene chloride/water partition coefficients (K_p).

Compound	K_p *(CH_2Cl_2/water)*
HMX	12.5
RDX	59.6
1,3,5-trinitrobenzene	299
1,3-dinitrobenzene	356
Nitrobenzene	352
2,4,6-trinitrotoluene	632
2,4-dinitrotoluene	681

was found for RDX using toluene. Hable et al. (1991) extended Belkin's method and found that good extraction efficiency for RDX and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) could be obtained using isoamyl acetate. Unfortunately, while good extraction efficiency was also obtained for the nitroaromatics using this solvent, unacceptably high interferences were introduced that could not be easily removed. Thus Hable et al. (1991) used two separate extractions and two separate determinations for nitroaromatics and nitramines, respectively.

The reason for the difficulty in obtaining good extraction efficiency, particularly for RDX and HMX, is their high polarity. This can be seen when comparing the octanol/water partition coefficients (K_{ow}) for a number of nitroaromatics and nitramines of interest (Table 2). K_{ow} values for HMX and RDX are 1.15 and 7.31, respectively, indicating the compounds are quite polar and will be difficult to extract from water using nonpolar solvents. Solvent/water partition coefficients using methylene chloride (Table 3), the solvent specified in many EPA procedures, are also low for HMX and RDX. Therefore methylene chloride is not an efficient extraction solvent for these compounds either.

Because of the difficulty in obtaining good extraction efficiency for HMX and RDX with conventional batch LLE, several alternative procedures were developed. The most successful of these have been the use of solid phase extraction (SPE) and salting-out liquid-liquid extraction (SOE).

Solid-phase extraction

As early as 1974, Junk et al. demonstrated the utility of resins such as XAD-2 and XAD-4 for the extraction of organic compounds from water. Anspach et al. (1982) evaluated 13 commercially available resins for their ability to sorb/desorb eight explosives (TNT, 2,4-DNT, 2,6-DNT, RDX, tetryl, PETN, nitroglycerine and picric acid). The materials tested included several styrene-divinylbenzene co-polymers, several acrylic esters, several carbonaceous materials, a polyvinylpyrrolidone, a polyvinylpyrridine, an acrylonitrile divinylbenzene copolymer, a C-18 reversed-phase silica, an activated carbon, and a reversed-phase cyanopropyl bonded material. Overall, Anspach et al. (1982) concluded that resins containing polyvinylpyrrolidone and polyvinylpyrridine (Porapak R and S, respectively) generally outperformed the other materials for preconcentration of the nitroaromatics, nitramines, nitrate esters and picric acid. Results for tetryl were the exception and in this case the styrene-divinylbenzene appeared to be superior. Maskarinec et al. (1984) compared the extraction efficiency of XAD-4 (a styrene-divinylbenzene polymer), Porapak R and Porapak S with classical LLE using methylene chloride and found improved recovery for HMX using the resins relative to LLE. Maskarinec and Anspach, however, both reported the presence of troublesome background impurities that interfered with UV detection after RP-HPLC separation. The composition of a number of the resins that have been

Table 4. Composition of various resins used for solid phase extraction of explosives from water.

Resin	*Composition*	*Polarity*	*Surface area* (m^2/g)
XAD-2	Styrene-divinylbenzene	Nonpolar	300
XAD-4	Styrene-divinylbenzene	Nonpolar	784
Porapak R	Divinylbenzene n-vinylpyrrolidine	Moderately polar	780
Porapak S	Divinylbenzene n-vinylpyridine	Polar	670
HayeSep R	Divinylbenzene (85%) n-vinyl-2-pyrollidone (15%)	Moderately polar	344
XAD-7	Acrylic ester	Moderately polar	450
Empore SDVB	Styrene-divinylbenzene	Nonpolar	

used for solid phase extraction of explosives is shown in Table 4.

Richard and Junk (1986) compared the recoveries of nitroaromatics and RDX on two styrene-divinylbenzene resins (XAD-2, XAD-4) and an acrylic ester resin (XAD-7). One liter samples were passed through the resin columns at 15 mL/min and the retained analytes desorbed with 20 mL of ethyl acetate. Good recovery (97–99%) was reported for XAD-4 (60–80 mesh) for water samples spiked with several nitroaromatics and RDX. Recovery of RDX from groundwater samples was shown to be comparable to LLE with methylene chloride, although as previously discussed, this solvent is not an efficient extractant for HMX and RDX.

Maskarinec et al. (1986) reported additional results comparing XAD-4, Porapak R and Porapak S. Water samples (500 mL) were pumped through the various resin tubes at 10-15 mL/min and the retained analytes eluted with 10 mL of acetone. Tetryl was found to be unstable in the acetone extract. This technique was used successfully at a number of Army installations. Detection limits were estimated at about 1 mg/L using RP-HPLC-electrochemical detection. The selectivity of the electrochemical detector for these analytes reduced the problem associated with coeluting interferences.

Bicking (1987) tested the method of Maskarinec et al. (1986) and made several modifications. Overall he found performance of the method was limited not by the SPE but by the method of determination (HPLC high performance liquid chromatography]–electrochemical detection).

Valis et al. (1989) also evaluated the resin SPE method developed by Maskarinec and confirmed that excellent recovery could be achieved using this approach. Both Valis and Bicking substituted HayeSep R, another commercial cross-linked divinylbenzene-polyvinylpyrrolidone polymer, for Porapak R (Table 4) and used UV and photoconductivity detectors rather than the electrochemical detector. Certified reporting limits (CRLs) obtained by Valis et al. (1989) and Bicking (1987) were comparable and ranged from about 0.8 µg/L for 2,4-DNT to about 7.5 µg/L for RDX. Higher CRLs were reported for tetryl, presumably because of the use of acetone for analyte elution from the resin.

Recently Winslow et al. (1991) reported a solid-phase extraction RP-HPLC-UV (reversed phase high performance liquid chromatography–ultraviolet detection) procedure for 15 nitroaromatic and nitramine analytes. Their procedure used Porapak R and they obtained CRLs ranging from 0.064 µg/L for 2,4-DNT to 2.49 µg/L for tetryl (Table 5). The method specifies passing a 500-mL water sample through a SPE cartridge containing 0.5 g of Porapak R at a flow rate of 10 mL/min. Recovery of the sorbed analytes used 3 mL of acetonitrile, which was a departure from previous work where a 10-mL volume of acetone was generally used. Recovery of the 15 analytes ranged from 84.1% for 4-nitrotoluene to 123% for 4-amino-2,6-dinitrotoluene with an overall mean recovery of 94.3%.

Winslow et al. (1991) packed their own SPE cartridges and reported that the packed cartridges were conditioned with 15 mL of acetonitrile and 30 mL of ASTM type II water. The Porapak R was extensively solvent cleaned prior to packing (1200 mL of acetone + 1200 mL of acetonitrile + 1200 mL

Table 5. Comparison of certified reporting limits for the solid-phase extraction procedure (Winslow et al. 1991) and salting-out solvent extraction procedures (Miyares and Jenkins 1990, 1991).

	CRL (µg/L)			
		Salting-out extraction		
Compound	Solid-phase extraction Winslow (1991)	Miyares and Jenkins (1990)	Winslow (1991)	Miyares and Jenkins (1991)
HMX	0.30	—	0.45	0.27
RDX	0.29	0.84	0.64	0.26
1,3,5-TNB	0.45	0.26	0.75	0.13
1,3-DNB	0.15	0.11	0.38	0.09
Tetryl	2.49	—	4.07	—
NB	0.65	—	4.4	—
2,4,6-TNT	0.64	0.11	0.57	0.011
4-Am-DNT	1.57	0.060	3.98	0.054
2-Am-DNT	0.16	0.035	0.86	0.056
2,6-DNT	0.074	0.31	0.123	0.006
2,4-DNT	0.064	0.021	0.088	0.007
2-NT	0.41	—	2.11	—
4-NT	0.62	—	2.07	—
3-NT	1.4	—	2.03	—

of methanol for each 75-cm^3 batch of Porapak R)*. If this cleaning procedure is used and a 75-cm^3 batch of Porapak R can fill about 40 tubes, the total solvent usage for cleaning and conditioning is more than 100 mL of solvent per cartridge (or per water sample).

Winslow et al. (1991) and Valis et al. (1989) both used cross-linked divinyl benzene-polyvinyl-pyrolidone resins for preconcentration of explosives but gave no explanation of the high efficiencies reported (Table 5). The high recoveries for HMX and RDX are surprising and cannot be explained by hydrophobic effects since their octanol/water partition coefficients are 1.15 and 7.31, respectively. This efficiency is probably due to formation of strong donor-acceptor complexes between HMX and RDX and the functionality of the polymer as described by Freeman et al. (1976).

SPE using Empore extraction disks

A new type of SPE extraction was introduced by Hagen et al. (1990), the Empore extraction disk. These disks are formed from a porous membrane of PTFE fibrils embedded with chromatographic particles. They are designed to be used with a vacuum filter flask and are claimed to maintain acceptable extraction efficiencies at maximum flow rates an order of magnitude greater than is acceptable for most SPE cartridges. The first membranes available contained particles of the reversed phase silicas. Initial tests using membranes containing C18 indicated poor recoveries (i.e., poor extraction efficiencies) for HMX and RDX. 3M Corporation recently developed Empore disks containing styrene-divinylbenzene particles. Markell† tested these disks for extraction efficiency of nitroaromatics and nitramines from ground and surface waters and found recoveries ranging from 49–122%.

Salting-out solvent extraction (SOE)

SOE for polar organic analytes was first reported by Leggett et al. (1990) and Miyares and Jenkins (1990). For SOE (version 1) a 130-g portion of NaCl is added to a 400-mL water sample in a 500-mL separatory funnel and shaken until the NaCl has completely dissolved. Once dissolved, a 100-mL volume of acetonitrile (ACN) is added and the sample is shaken for 5 minutes. The sample is allowed to stand for 30 minutes to permit phase separation and the upper ACN layer is retained. After Kuderna-Danish concentration and dilution with water, the preconcentrated extract is analyzed by RP-HPLC-UV. Miyares and Jenkins (1990) reported recoveries ranging from 89% to 137% for eight nitroaromatic and nitramine analytes, with CRLs ranging from 0.021 for 2,4-DNT, to 0.84 µg/L for RDX (Table 5).

More recently, Miyares and Jenkins (1991) reported an improved salting-out extraction procedure (SOE version 2) where 248 g of NaCl is dis-

*M.G. Winslow, ESE, Gainsville, Florida, personal communication, 1992.

† C.G. Markell, 3M Corporation, St. Paul, Minnesota, personal communication, 1992.

solved in a 760-mL water sample in a 1-L volumetric flask and 170-mL of ACN added. The solution is stirred for 30 minutes. The ACN phase (about 23 mL) is removed with a Pasteur pipet and the remaining solution is extracted with an additional 10 mL of ACN. The two ACN extracts are combined and evaporated to about 0.5 mL using a Kuderna-Danish evaporator. The sample is diluted with water up to about 2.0 mL, allowed to reflux briefly to allow further reduction of the ACN and then combined with 3.00 mL of water. The resulting extract is analyzed by RP-HPLC-UV. Certified Reporting Limits for this method (Table 5) ranged from 0.006 mg/L for 2,6-DNT to 0.271 µg/L for HMX. Recoveries ranged from 63.0% for 1,3,5-trinitrobenzene to 118% for HMX.

One drawback to this procedure is the need to preconcentrate the 33-mL ACN extract. Kuderna-Danish evaporation of ACN is slow, requiring that the extract be heated for an extended period. Since many explosive analytes are thermally unstable, this procedure is less than ideal. In addition, evaporative preconcentration is felt by many, including the authors, to be a major source of quantitative uncertainty in trace organic analysis.

Recently a new procedure was published for preconcentrating ACN extracts without using evaporation (Jenkins and Miyares 1991). This procedure is based on favorable partitioning of organic solutes between salted-out ACN and salt water. To use this procedure, the appropriate volume of ACN (a small excess above the solubility) is added to a known volume of salt water in a volumetric flask and the solution stirred vigorously. After equilibration, the phases are allowed to separate and the small-volume ACN phase residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. Use of this procedure to preconcentrate the ACN extract from the salting-out extraction is an attractive option.

Comparisons of SPE and SOE

Winslow et al. (1991) compared their SPE method with the SOE method (version 1) of Miyares and Jenkins (1990). Winslow obtained slightly better CRLs (Table 5) and better recoveries (Table 6) using SPE. Winslow also concluded that the SPE procedure was less time consuming than the SOE.

Miyares and Jenkins (1991) attempted a direct comparison between their improved SOE method (version 2) and the SPE method of Valis et al. (1989). The concentrations of the nitroaromatics and nitramines were an order of magnitude lower than tested by Winslow et al. (1991) or Valis (1989), and interferences from compounds leached from the resin were observed at the absorbances needed to detect these lower concentrations. The HayeSep R cartridges were precleaned by passing 50 mL of acetonitrile through the resin cartridges at 10 mL/min followed by 100 mL of reagent grade water at 10 mL/min. This treatment appears to be inadequate if very low concentrations (< 1 µg/L) are to be determined.

Table 6. Percent recoveries for nitroaromatics and nitramines obtained by Winslow et al. (1991) using SPE and SOE.

	% Recovery (mean ±std dev)	
Compound	*SPE*	*SOE*
HMX	97.8 ± 4.1	91.8 ± 5.5
RDX	95.5 ± 6.6	86.7 ± 6.2
1,3,5-TNB	84.7 ± 16.0	70.8 ± 18.6
1,3-DNB	971 ± 6.5	83.9 ± 8.6
Tetryl	91.1 ± 11.6	80.1 ± 14.5
NB	92.7 ± 7.0	81.5 ± 9.1
2,4,6-TNT	96.8 ± 12.6	89.4 ± 14.1
4-Am-DNT	123 ± 18.3	126 ± 19.1
2-Am-DNT	92.2 ± 12.4	78.4 ± 11.2
2,6-DNT	90.3 ± 11.0	83.6 ± 12.8
2,4-DNT	85.2 ± 9.1	76.7 ± 9.9
2-NT	91.9 ± 8.0	76.6 ± 7.3
4-NT	84.1 ± 10.0	75.1 ± 7.1
3-NT	90.8 ± 12.6	77.3 ± 11.1

Objective

The objective of the work described here was to obtain a direct comparison of the cartridge SPE method of Winslow et al. (1991) and the membrane SPE method of Markell* with the improved SOE method of Miyares and Jenkins (1991) utilizing the nonevaporative preconcentration procedure of Jenkins and Miyares (1991). Aqueous test solutions of nitroaromatics and nitramines prepared in groundwater without the use of organic solvents allowed a realistic comparison at concentrations of analytes below the proposed drinking water criteria (Table 1). Methods were also compared in terms of solvent requirements, waste production and processing time. In addition all three procedures were tested with a set of groundwater samples from a military toxic waste site known to be contaminated with nitroaromatic and nitramine explosives.

* C.G. Markell, 3M Corporation, St. Paul, Minnesota, personal communication, 1992.

EXPERIMENTAL

Conduct of study

This study was conducted jointly by the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire, and the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi. Preliminary experiments and Certified Reporting Limit (CRL) tests were conducted at CRREL. Tests using groundwater samples from the Rockeye site at the Naval Surface Warfare Center, Crane, Indiana, were conducted at WES. The RP-HPLC instrumentation used at the two laboratories is specified below.

Salting-out solvent extraction/nonevaporative preconcentration procedure

This method was based on the salting-out solvent extraction procedure reported by Miyares and Jenkins (1991) (SOE version 2) in combination with the nonevaporative preconcentration technique reported by Jenkins and Miyares (1991). A 251.3-g portion of reagent grade sodium chloride was added to a 1-L volumetric flask. A 770-mL sample of water was measured with a 1-L graduated cylinder and added to the flask. A stir bar was added and the contents stirred at maximum speed (rpm) until the salt was completely dissolved. A 164-mL aliquot of ACN (measured with a 250-mL graduated cylinder) was added while the solution is being stirred and stirring was continued for 15 minutes. The stirrer was turned off and the phases allowed to separate for 10 minutes. The ACN phase (about 8 mL) was removed and 10 mL of fresh ACN added. The flask was again stirred for 15 minutes, followed by 10 minutes for phase separation. The ACN was removed and combined with the initial extract. The inclusion of a few drops of salt water at this point is unimportant. The extract was placed in a 100-mL volumetric flask and 84 mL of salt water (325 g NaCl per 1000 mL of water) was added. A stir bar was placed in the flask and the contents stirred for 15 minutes. After allowing the phases to separate for 10 minutes, the ACN phase was carefully removed using a Pasteur pipet and placed in a 10-mL graduated cylinder. (At this stage the amount of water transferred with the ACN must be minimized because the water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram where it could interfere with HMX determination.) An additional 1.0-mL aliquot of ACN was then added to the volumetric flask and the contents stirred for 15 minutes. Again the phases were allowed to separate for 10 minutes and the resulting ACN phase was added to the 10-mL graduated cylinder. The resulting extract, about 5–6 mL, was than diluted 1:1 with reagent grade water prior to analysis.

Cartridge solid-phase extraction

This procedure was taken from Winslow et al. (1991). Porapak R (80/100 mesh) was obtained from Supelco. In order to reduce solvent consumption, we precleaned this bulk material by Soxhlet extraction using ACN. Two 300-mL portions of ACN were each used for a period of 1 day per 75 cm^3 portion of polymer. After precleaning, the material was air dried briefly and then oven dried at 105°C for 2 hrs.

Empty 3-mL extraction cartridges were fitted with 20-µm frits at the bottom and packed with 0.5 g of the precleaned Porapak R. Another frit was placed on top to retain the material and help minimize channeling. The cartridges were placed on a Visiprep Solid-Phase Extraction Manifold (Supelco) and conditioned by eluting with 30 mL of ACN by gravity flow followed by 50 mL of reagent grade water at 10 mL/min. A 500-mL aliquot of each water sample was measured with a 1-L graduated cylinder and pulled through a cartridge at about 10 mL/min.

The cartridges were eluted by passing a 5-mL aliquot of ACN through the cartridge at about 2 mL/min and the eluate collected in a 10-mL graduated cylinder. The resulting extract, about 5 mL, was diluted 1:1 with reagent grade water prior to analysis.

Membrane solid-phase extraction

The 47-mm Empore styrene-divinyl benzene disks were precleaned by soaking each disk in a 250-mL beaker containing a layer of glass beads (5 mm) and 50 mL of ACN. Each membrane was soaked for 24 hours, then washed off with ACN and transferred to a second beaker of ACN. Membranes were each subjected to four 24-hour periods of soaking in fresh ACN. Each disk was rinsed with ACN, then centered on a 47-mm vacuum filter apparatus. A 20-mL portion of ACN was added and allowed to soak into the disk for 3 minutes. The vacuum was then turned on and most of (but not all) the solvent pulled through the disk. A 50-mL aliquot of reagent grade water was then added and the vacuum was turned on, pulling the water through the membrane. Just before the last of this water was pulled through the membrane, the vacuum was stopped and the reservoir filled with

sample. The vacuum was then turned on again and a 500-mL aliquot of a water sample was pulled through the membrane. This took from 5 to 7 minutes, with resulting flow rates ranging from 70 to 100 mL/min. Once the water was exhausted, air was drawn through the membrane for one minute to remove excess water. The vacuum was then turned off and the vacuum flask removed. The water was removed from the flask and a test tube placed in the flask such that it fit over the funnel exit when the flask was reattached to the fritted base. The actual size of the test tube needed depends on the brand of vacuum flask used (25 x 200 mm or 25 x 250 mm). A 5-mL aliquot of ACN was added to the reservoir, the ACN allowed to soak into the membrane for 3 minutes and then the vacuum was applied to pull the ACN through the membrane into the test tube. The resulting extract was then removed with a Pasteur pipet and placed in a 10-mL graduated cylinder. An appropriate portion of reagent grade water (< 5.0 mL) was added to the test tube. This water was used to dilute the ACN extract 1:1 prior to analysis.

RP-HPLC analysis

CRREL RP-HPLC analysis

All analyses were conducted using reversed-phase HPLC. Samples were analyzed on a modular system composed of a Spectra Physics 8800 pump, a Dynatech Precision Sampling LC-241 autosampler equipped with a Rheodyne Model 7010 A sample loop injector, a Spectra Physics Spectra 100 variable wavelength detector set at 254 nm, a Hewlett-Packard HP 3393A digital integrator and Linear strip chart recorder. Primary separations used a 25-cm x 4.6-mm LC-18 (5-µm) column eluted with 1:1 methanol/water at a flow rate of 1.5 mL/min (Jenkins et al., 1989). Samples were introduced through the autosampler by overfilling a 100-µL loop. If primary analysis indicated that nitroaromatic or nitramine analytes could be present, second column confirmation was obtained on a combined LC-8/LC-CN column (Miyares and Jenkins 1991). Retention times for the various nitroaromatic and nitramine analytes using these two separations are shown in Table 7.

Table 7. Retention times for various analytes using two RP-HPLC separations.

	Retention time (min)	
Analyte	*LC-18**	*LC-8/LC-CN***
HMX	2.5	3.8
RDX	3.8	3.4
TNB	5.1	2.3
DNB	6.1	3.1
Tetryl	6.9	7.2
TNT	8.2	4.5
2,6-DNT	9.6	6.3
2,4-DNT	9.8	5.7
4-Am-DNT	8.9	8.4
2-Am-DNT	9.1	8.0
2-NT	11.7	6.8
4-NT	12.6	6.9
3-NT	13.5	7.5

* LC-18 (25-cm x 4.6-mm, 5-µm) column eluted with 1.5 mL/min of 1:1 (v/v) methanol/water.

** LC-8 (3.3 cm x 4.6 mm, 3 µm) column connected in series with a LC-CN (3.3-cm x 4.6-mm, 3-µm) column eluted with 70.7:27.8:1.5 (v/v/v) water/methanol/tetrahydrofuran at 1.5 mL/min.

b. WES RP-HPLC analysis

Analyses of the groundwater samples from the Naval Surface Warfare Center were conducted in two ways at WES. First the samples were analyzed directly by dilution 1:1 with methanol, filtration through a Millex SR disposable membrane filter and determination of a 100-µL aliquot on a LC-18 column (Supelco 25 cm x 4.6 mm, 5 µm) eluted with 1:1 methanol/water at a flow rate of 1.2 mL/min. This analysis was conducted on a Waters HPLC consisting of a 600 MS System Controller, a 700 Satellite WISP injector, and a 991 MS Photodiode Array Detector set to monitor in the range 220–260 nm (calibration at 254 nm). If analytes appeared to be present, second column confirmation was obtained on an LC-CN column (Jenkins et al., 1989). Retention times obtained for the two columns are given in Table 8.

Table 8. Retention times for direct water analysis conducted at WES.

	Retention time (min)	
Analyte	*LC-18**	*LC-CN***
HMX	3.8	16.0
RDX	5.4	10.2
TNB	7.1	6.4
DNB	8.4	6.3
Tetryl	9.6	12.9
TNT	11.3	7.9
4-Am-DNT	12.4	8.6
2-Am-DNT	12.7	9.2
2,6-DNT	13.2	7.2
2,4-DNT	13.4	7.5

* LC-18 column (25 cm x 4.6 mm, 5 µm) eluted with 1:1 (v/v) methanol/water at 1.2 mL/min.

** LC-CN column (25 cm x 4.6 mm, 5 µm) eluted with 1:1 (v/v) methanol/water at 1.0 mL/min.

Table 9. Preparation of test samples.

Analyte	Concentration combined standard (µg/L)	Combined spike solution (µg/L)	Test sample 0.5X Vol. added* (mL)	0.5X Conc. (µg/L)	1X Vol. added (mL)	1X Conc. (µg/L)	2X Vol. added (mL)	2X Conc. (µg/L)	5X Vol. added (mL)	5X Conc. (µg/L)	10X Vol. added (mL)	10X Conc. (µg/L)
HMX	227	45.1	5.00	0.057	10.00	0.114	20.0	0.227	50.0	0.568	100.0	1.14
RDX	207	41.4		0.052		0.104		0.207		0.518		1.04
TNB	165	33.0		0.041		0.082		0.165		0.412		0.82
DNB	209	41.7		0.052		0.104		0.209		0.522		1.04
Tetryl	184	36.8		0.046		0.093		0.190		0.460		0.93
TNT	196	39.2		0.049		0.098		0.196		0.490		0.98
2-Am-DNT	208	41.7		0.052		0.104		0.208		0.521		1.04
24-DNT	201	40.3		0.050		0.101		0.201		0.503		1.01
o-NT	214	42.9		0.054		0.107		0.214		0.536		1.07
p-NT	213	42.5		0.053		0.106		0.213		0.531		1.06
m-NT	247	49.3		0.062		0.123		0.247		0.616		1.23

* Volume of combined standard added to 4.0 L of ground water and resulting concentration.

Samples were also preconcentrated by each of the three procedures described above (SOE, membrane SPE and cartridge SPE). A 100-mL volume of each preconcentrated extract diluted 1/1 with water was analyzed at WES on an LC-18 (Supelco 25 cm × 4.6 mm, 5 µm) column eluted with 1:1 methanol/water at 1.5 mL/min. These analyses were conducted on a Waters HPLC consisting of a 600 E System Controller/Multi Solvent Delivery System, a 712 WISP sample injector, and a 486 Tunable Absorbance Detector set at 254 nm. Retention times for the analytes of interest were similar to those presented in Table 7. Confirmations of analyte identities were conducted at CRREL as described above.

Preparation of standards and samples

Since we felt it was important that test samples be completely free of organic solvents, particularly those to be preconcentrated using solid phase extraction, we prepared all test samples at CRREL in a totally aqueous matrix. This was done by preparing individual aqueous analyte stock solutions by placing a few hundred milligrams of Standard Analytical Reference Material (SARM) of each specific analyte in individual 4-L brown glass bottles, filling with reagent grade water, adding a stir bar and stirring for two days at room temperature.

Each solution was filtered through a 0.45-µm nylon-66 membrane (Supelco) into a clean brown glass bottle. Aliquots of each solution were then analyzed against standards prepared in acetonitrile to estimate the concentration of analyte in each aqueous stock solution.

A combined standard with analyte concentrations of about 200 µg/L was prepared by adding various volumes of the individual stock solutions in a 500-mL volumetric flask and diluting to volume with reagent grade water (Table 9). An aliquot of this solution was diluted using reagent grade water to prepare the combined spike solution with analyte concentrations of approximately 40 µg/L (Table 9).

Test samples (0.5 to 10X) were prepared from this combined solution by diluting various volumes of the combined standard to 4.0 L using reagent grade water (Table 9).

RESULTS AND DISCUSSION

Preliminary experiments—SOE

One parameter in both the salting-out extraction (SOE) procedure (Miyares and Jenkins, 1991) (SOE version 2) and the nonevaporative preconcentration technique that has not been systematically studied is the stirring time required to reach equilibrium between the two phases. Times of 30 minutes and 3 hours, respectively, were specified but no specific studies were conducted to optimize this parameter. To do so, we prepared an aqueous solution of 10 of the analytes of interest (Table 10) and performed a salting-out solvent extraction (SOE version 2) as specified in the *Experimental* section. After 10, 20 and 30 minutes, the stirrer was stopped, the phases allowed to separate, and an aliquot of the ACN extract analyzed (Table 10). Results indicate that transfer of the analytes to the ACN phase was complete within the initial 10-minute stirring period. Stirring in this experiment was conducted at the maximum speed (rpm) of our magnetic stirrer. This created a vortex throughout the flask and intimate contact between the phases. Because the degree of phase contact could be somewhat different from unit to unit, we recommend a 15-minute stirring time at maximum speed.

A similar experiment was conducted to optimize the stirring time for the reverse process used in the nonevaporative preconcentration of the ACN extract. In principle, the reverse process should attain equilibrium at the same rate as observed above. Nevertheless, we decided to confirm this experimentally. To do so, a 18-mL aliquot of an ACN standard containing analytes (Table 11) was added to a 100-mL volumetric flask containing 84 mL of salt water (325 g NaCl per 1000 mL of water) and the contents stirred for 10, 20 and 30 min. After each time increment, a small aliquot of the extract was removed and analyzed as usual

Table 10. Results of stirring time study for salting-out extraction (version 2).

Analyte	*Initial aqueous concentration (µg/L)*	*Concentration in ACN extract (µg/L)*		
		10 min	*20 min*	*30 min*
HMX	27.3	2520	2410	2530
RDX	26.7	1840	1810	1860
TNB	24.6	2270	2200	2290
DNB	26.3	2120	2060	2140
Tetryl	26.1	2940	2820	2990
TNT	25.3	2710	2600	2760
2-AmDNT	27.8	2480	2400	2510
2,4-DNT	20.6	2000	1930	2030
p-NT	32.7	3090	2950	3100
m-NT	30.3	2930	2790	2940

Table 11. Results of stirring time study for nonevaporative preconcentration step.

Analyte	Initial concentration in ACN (µg/L)	Concentration in ACN phase after stirring (µg/L)			
		10 min	20 min	30 min	90 min
HMX	106	628	657	590	601
RDX	102	673	776	569	564
TNB	107	591	598	584	591
DNB	100	534	543	532	535
Tetryl	102	577	585	580	569
TNT	107	614	623	605	599
2-ADNT	108	598	609	601	600
2,4-DNT	102	618	605	562	569
o-NT	102	561	571	567	560
p-NT	100	560	567	557	565
m-NT	101	567	562	559	565

(Table 11). While these data are somewhat less precise than normal due to the need to inject small volumes into a large sample loop, the results indicate that equilibrium is achieved within 10 minutes for all analytes. Again, we recommend a 15-minute stirring time at maximum speed.

Preliminary experiments—cartridge SPE

As discussed in the *Introduction*, both Porapak R and HayeSep R have been used with apparent success for preconcentration of nitroaromatic and nitramine explosives using cartridge SPE. We obtained both materials from Supelco. Some of the characteristics of both materials are presented in Table 12.

We were uncertain as to which of these materials would be the best choice for our application. Two criteria were important in this regard: sorption capacity and material cleanliness. With respect to the latter, ACN extracts of both materials were obtained and analyzed by both RP-HPLC and GC/MS. The HayeSep R material was much cleaner than Porapak R, although both contained contaminants that would interfere with RP-HPLC analysis for nitroaromatic and nitramine explosives. A variety of cleaning techniques and solvents were examined, and it appears that the contaminants are slowly leached from the interior of the polymeric material by diffusion. Thus, cleaned material can appear "clean" if examined immediately after solvent cleaning, but upon standing, the contaminants reappear. We concluded that it was not the amount of solvent used to clean the material that was limiting, but rather the amount of contact time with periodic solvent replacement. Soxhlet extraction for two days using ACN proved to be adequate. Since both materials could be cleaned adequately, the initial cleanliness advantage of HayeSep R was not critical.

To examine the other criterion, sorption capacity, we measured polymer/water partition coefficients for various nitroaromatics and nitramines on both HayeSep R and Porapak R. This was done by accurately weighing out 131 mg of the previously cleaned and dried material of interest into a clean 40-mL Teflon-capped glass vial and adding 20.00 mL of aqueous solution containing a series of nitroaromatics and nitramines. The vials were shaken on a wrist action shaker for 72 hours. Concentrations of the various sorbates in aqueous solu-

Table 12. Characteristics of Porapak R and HayeSep R SPE polymers.

Parameter	HayeSep R	Porapak R
Mesh size	80/100	80/100
Specific surface area (m^2/g)	344*	450/600*

* Information provided by Lydia Nolan, Supelco, Inc., 1992.

Table 13. Polymer/water partition coefficients.

Sorbate	$\log K_p$	
	HayeSep R	Porapak R
HMX	2.15	2.40
RDX	3.10	3.10
TNB	4.65	4.29
DNB	4.74	4.48
2,6-DNT	5.55	5.38
2-Am-DNT	4.99	4.86

tion (solutions prepared without use of organic solvent) were measured before and after equilibration with each polymer and the concentration of sorbates on the polymer obtained by difference. The partition coefficients (K_p) in g/g were then calculated (Table 13). HMX is the least well sorbed by these materials. Of the two polymers, HMX is sorbed somewhat better by Porapak R but overall there is very little difference. Tests with other materials such as Porapak Q (styrene-divinylbenzene polymer) and LC-18 (octadecyl bonded reversed phase silica) indicate that these materials have lower polymer/water partition coefficients and thus are even poorer choices. Thus Porapak R was selected for use in cartridge SPE because it did sorb HMX to a greater extent and allowed a direct comparison of the study conducted by Winslow et al. (1991).

Certified reporting limit test

The test solutions shown in Table 9 were used to conduct a 4-day Certified Reporting Limit Test as described in USATHAMA (1990). This test provides a means to compare the performance of the three preconcentration methods with regard to low concentration detection capability, percent recovery, interferences and overall precision.

The test was conducted by preparing the test solutions at various concentrations, designated blank, 0.5X, X, 2X, 5X and 10X (Table 9), on each of four days, where X represents a concentration near the detection limit. An aliquot of each solution was preconcentrated using the salting-out, cartridge-SPE and membrane-SPE procedures described in the *Experimental* section. The extracts on a given day were randomized prior to analysis at CRREL using the RP-HPLC method described in the *Experimental* section.

Examples of the chromatograms we obtained for the blank and 2X samples for each of the three preconcentration methods are shown in Figures 2 and 3, respectively. The determined concentrations for each extract are presented in the Tables A1–A33. To obtain the CRL for each analyte using each preconcentration technique, the found vs. spiked concentrations over the four days are plotted and a linear least-squares regression model with intercept is fitted. Confidence intervals about the regression lines are obtained at the 90% confidence level (5% a risk, 5% b risk). A horizontal line is drawn from the intersection of the upper confidence band and the *y*-axis until it intersects the lower confidence band. A vertical line is dropped to the *x*-axis and the intersection defined as the CRL

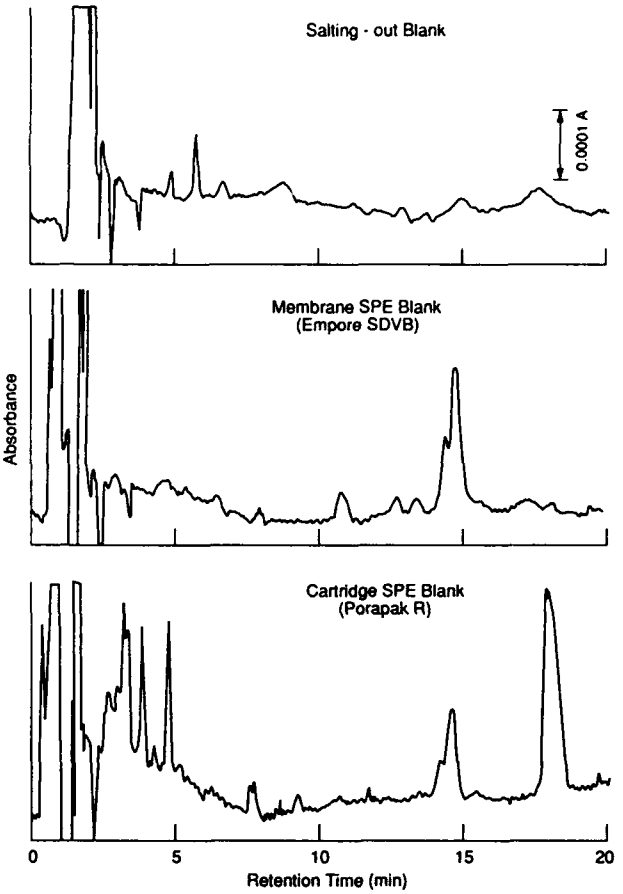

Figure 2. LC-18 chromatograms for blank sample preconcentration by salting-out, cartridge-SPE and membrane-SPE methods at CRREL.

(Hubaux and Vos 1970). A graphical illustration of this procedure is presented in Figure 4. CRLs for each analyte using salting-out, cartridge-SPE and membrane-SPE are presented in Table 14.

Table 14. Certified reporting limits for various preconcentration techniques.

	CRL (µg/L)		
Analyte	*Salting-out*	*Cartridge-SPE*	*Membrane-SPE*
HMX	0.19	0.21	0.33
RDX	0.13	0.27	0.12
TNB	0.052	0.042	0.051
DNB	0.081	0.032	0.036
Tetryl	0.20	0.24	0.83
TNT	0.086	0.068	0.13
2-Am-DNT	0.10	0.046	0.055
2,4-DNT	0.083	0.085	0.044
o-NT	0.13	0.10	0.20
p-NT	0.22	0.12	0.23*
m-NT	0.21	0.13	0.37

* One outlier removed for this analyte/method combination.

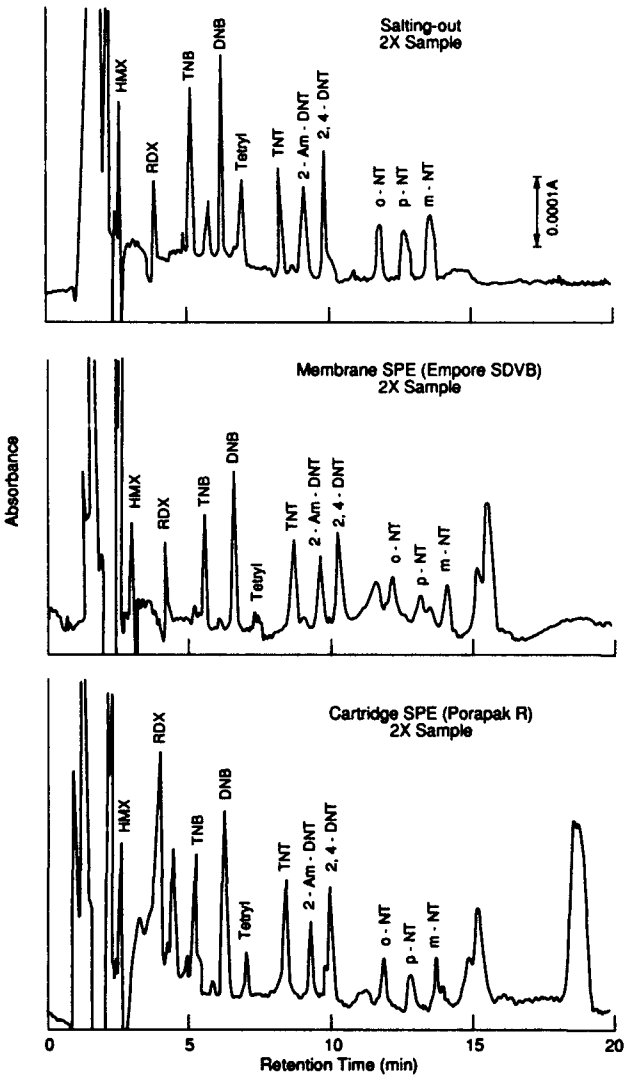

Figure 3. LC-18 chromatograms for 2X sample preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at CRREL.

Overall the CRLs for a given analyte are quite similar for all three preconcentration techniques. None of the procedures are consistently superior to the others in low concentration detection capability. CRL values range from a low of 0.032 µg/L for DNB using cartridge SPE, to a high of 0.83 µg/L for tetryl using membrane-SPE. All values for HMX, RDX, TNT, 2,4-DNT and 1,3-DNB are below the proposed drinking water limit for these compounds. While 2,6-DNT was not tested, it is very unlikely that a CRL as low as the proposed value of 0.007 µg/L would be obtained. The only CRL value that appears to be out of line is the 0.83 µg/L value of tetryl using membrane-SPE. Inspection of the data indicates this high CRL is due to low recovery on one of the four days (Table A27).

The regression line obtained from the plot of found vs. spiked concentrations was also examined for curvature using lack-of-fit testing. A linear relationship adequately described the data at the 95% confidence level for all the analytes using all three procedures with the exception of p-NT by the cartridge SPE method. The slopes of these linear regression lines are measures of the overall percent recoveries of these analytes using each preconcentration method. Recoveries (Table 15), in general, are quite good (near a theoretical value of 100%). Measured recoveries for the salting-out procedure range from 93–119%. Likewise recoveries for cartridge-SPE and membrane-SPE range from 83–133% and 81–116%, respectively.

The *y*-intercept values from the regression equations were tested to determine if they were significantly different from 0 at the 95% confidence level. Statistically significant intercept val-

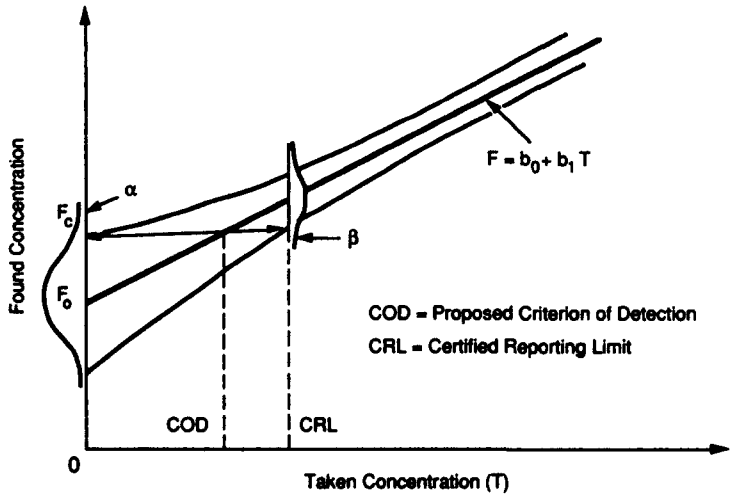

Figure 4. Graphical illustration of CRL procedure.

ues are presented in Table 16. These values are quite low for all three procedures. Except for RDX by the cartridge SPE procedure, these values are lower than the CRLs for that specific compound. Thus positive interferences are not generally of practical importance for any of these preconcentration techniques. The intercept for RDX using cartridge SPE was 0.35 and the CRL was 0.27 µg/L. In this case, a positive interference was found and was consistently noted in the chromatograms of the blank sample (Table A2). This interference was also observed for the membrane-SPE for RDX. These were the only analyte/method combinations where found values were consistently observed for the blank sample. For the membrane, the blank values obtained for RDX were slightly below the CRL obtained for RDX.

Comparison using groundwater samples

Since all three preconcentration techniques performed adequately using spiked reagent water samples, a further test was conducted using ground water samples from the Rockeye site at the Naval Surface Warfare Center. Samples were collected using a Grundo Rediflo 2 stainless steel submersible pump at about 100 mL/min after the well was developed and allowed to recharge. Four liters of groundwater from each well was shipped to WES in glass ICHEM bottles. All of the groundwater samples collected were analyzed by the direct method at WES (Jenkins et al. 1988). A subset of 58 of these groundwater samples were also preconcentrated using the three procedures (SOE, cartridge-SPE and membrane-SPE) and analyzed at WES as described above. Table 17 summarizes the results for samples where the concentrations of at least one nitroaromatic or nitramine analyte was high enough to be obtained using the direct method. Since the concentrations obtained by the direct analysis are subject to fewer sources of error than those obtained using preconcentration, we are treating these values as "true" values for purposes of comparison. We can then compare the results from the various preconcentration techniques relative to these "true" values.

Examination of Table 17 indicates that all three preconcentration procedures did a fairly good job of obtaining results similar to those from the direct analysis. Regression analysis was conducted on the results obtained for HMX, RDX and TNT by the direct method vs. the three preconcentration techniques. The theoretical relationship expected is $y = 1.0X$, if there is no bias. The slope (m), y-intercept (b) and square of the correlation coefficient (r^2) for each analysis are presented in Table 18. Clearly the slopes obtained for the membrane-SPE method indicate this method recovered less of HMX and RDX than the other two procedures. A lower recovery for HMX is consistent with the results obtained on the spiked reagent water samples at CRREL. However, a slope of 0.491 (49.1% recovery) is much poorer than the 81% recovery obtained on the spiked water samples at CRREL. There are several possible explanations for this lower recovery. The concentration of HMX in the groundwater samples

Table 15. Overall percent recovery and relative standard deviation (RSD) from Certified Reporting Limit Test.

	% Recovery* (% RSD)		
Analyte	*Salting-out*	*Cartridge-SPE*	*Membrane-SPE*
HMX	106 (10.5)	107 (9.6)	81 (14.0)
RDX	106 (8.7)	116 (22.0)	116 (11.1)
TNB	119 (7.6)	133 (8.7)	116 (10.3)
DNB	102 (6.6)	115 (2.6)	103 (6.5)
Tetryl	93 (16.4)	83 (32.8)	83 (46.4)
TNT	105 (7.6)	111 (7.5)	97 (10.5)
2-Am-DNT	102 (9.1)	113 (4.1)	103 (8.9)
2,4-DNT	101 (5.8)	109 (6.8)	94 (6.6)
o-NT	102 (9.1)	107 (8.1)	92 (15.6)
p-NT	96 (18.1)	104** (6.6)	89† (18.0)
m-NT	97(12.4)	100 (7.3)	86 (17.2)

* Slope of regression line of spiked concentration vs. found concentration × 100.

** Lack-of-fit test indicates data not adequately described by linear relationship at the 95% confidence level.

† One outlier removed for this analyte/method combination.

Table 16. Y intercepts for regression lines for spiked vs. found concentrations in 4-Day CRL test.

	Y Intercept (µg/L)		
Analyte	*Salting-out*	*Cartridge-SPE*	*Membrane-SPE*
HMX	0.123	0.148	0.149
RDX	0.052	0.350	0.053
TNB	0.029	NS*	0.022
DNB	NS	0.009	NS
Tetryl	0.045	NS	NS
TNT	0.032	0.053	0.049
2-Am-DNT	0.040	0.015	NS
2,4-DNT	0.024	0.032	NS
o-NT	0.046	NS	0.055
p-NT	0.080	**	NS†
m-NT	0.054	NS	0.100

* NS-Intercept not significantly different from 0 at the 95% confidence level.

** Linear model was not adequate to describe spiked vs. found relationship at the 95% confidence level.

† One outlier removed for this analyte/method combination.

Table 17. Comparison of results for direct analysis of groundwater samples from the Rockeye site at the Naval Surface Warfare Center, Crane, Indiana, with the three preconcentration methods.

		Concentration (µg/L)				
Sample	*Method**	*HMX*	*RDX*	*TNB*	*TNT*	*4A*
20649	Direct	151	135		33	9.6
	SPE-M	98	121		32	11.2
	SPE-C	156	147		34	12.2
	SOE	161	138		38	13.7
20650	Direct	119	82		9.0	
	SPE-M	60	64		7.6	
	SPE-C	107	85		9.2	
	SOE	98	66		10.3	
20660	Direct		26			
	SPE-M		23			
	SPE-C		24			
	SOE		21			
20661	Direct	70	37			
	SPE-M	74	55			
	SPE-C	98	58			
	SOE	93	56			
20662	Direct	26	160		42	
	SPE-M	19	176		51	
	SPE-C	17	138		34	
	SOE	22	154		46	
20663	Direct	281	94		21	65
	SPE-M	153	89		22	75
	SPE-C	214	109		26	78
	SOE	232	90		26	78
20667	Direct	318	618	19.2	284	166
	SPE-M	199	488	19.5	317	216
	SPE-C	356	666	19.6	328	239
	SOE	319	558	18.6	320	217

* Membrane-SPE (SPE-M), Cartridge-SPE (SPE-C) and Salting-out (SOE).

Table 18. Results of regression analysis of the straight analysis versus the three preconcentration methods for groundwater samples from Rockeye site, Naval Surface Warfare Center.

	Analyte								
	HMX			*RDX*			*TNT*		
Method	m*	b**	r^2	m	b	r^2	m	b	r^2
Membrane–SPE	0.491	17.5	0.947	0.769	18.6	0.988	1.12	–1.4	0.999
Cartridge–SPE	0.873	10.4	0.935	1.07	–0.8	0.994	1.17	–4.6	0.997
SOE	0.812	16.9	0.967	0.892	7.9	0.996	1.12	0.6	1.000
Membrane–SPE	0.491	17.5	0.947	0.769	18.6	0.988	1.12	–1.4	0.999
Cartridge–SPE	0.873	10.4	0.935	1.07	–0.8	0.994	1.17	–4.6	0.997
SOE	0.812	16.9	0.967	0.892	7.9	0.996	1.12	0.6	1.000

* *m*—slope
** *b*—Y intercept

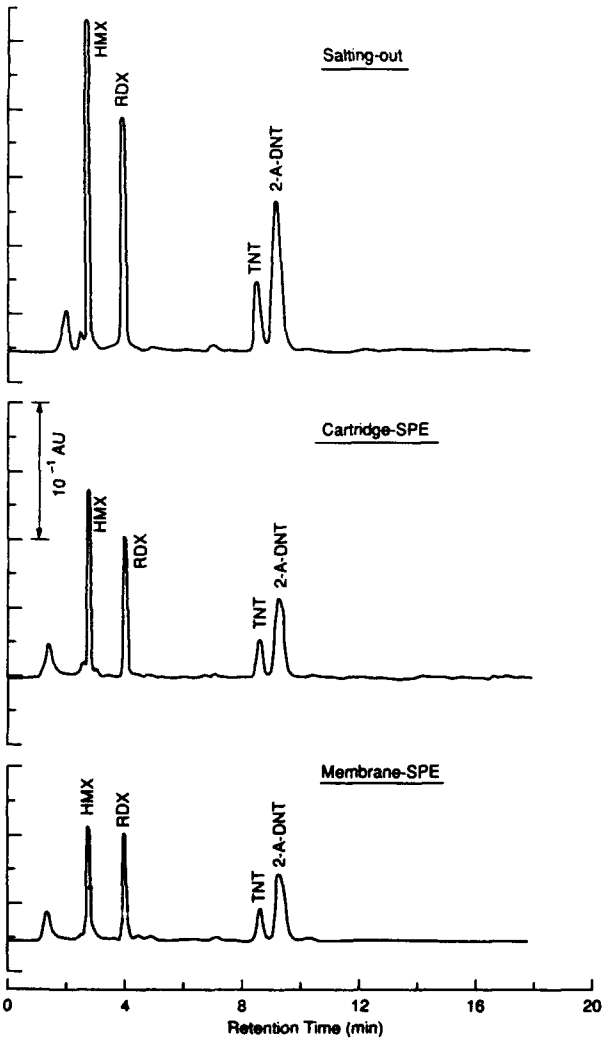

Figure 5. LC-18 chromatograms for sample 20649 from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at WES.

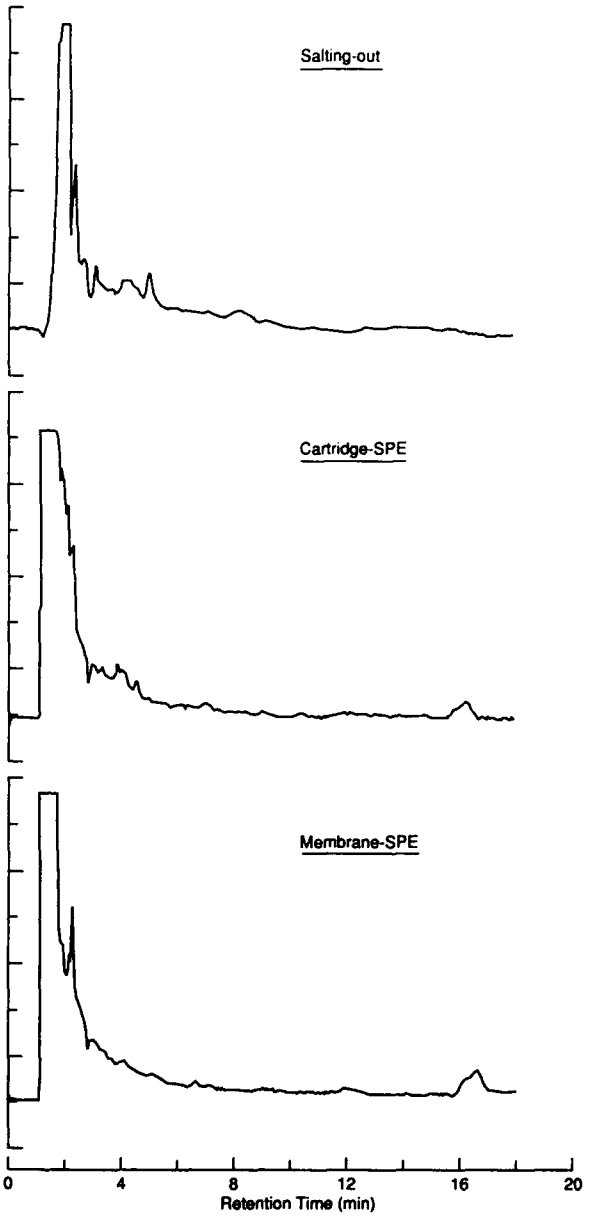

Figure 6. LC-18 chromatograms for sample 20670 from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at WES.

from the Rockeye site were 15–320 times greater than the highest concentrations tested in the spiked reagent water samples. This higher mass loading could have exceeded the capacity of the membrane for this solute. A lower recovery value for Rockeye samples could also be caused by the presence of particles in the groundwater samples, which could block some of the pores in the membrane causing flow to be less uniform across the surface of the membrane. Larger volumes passing through certain regions and hence a greater breakthrough of HMX would result in those zones of preferential flow.

Recovery of HMX, RDX and TNT by the cartridge-SPE and salting-out methods were greater than 80% in all cases with a slightly better recovery for the cartridge-SPE method for HMX and RDX.

Inspection of the chromatograms obtained for the samples from the three different preconcentra-

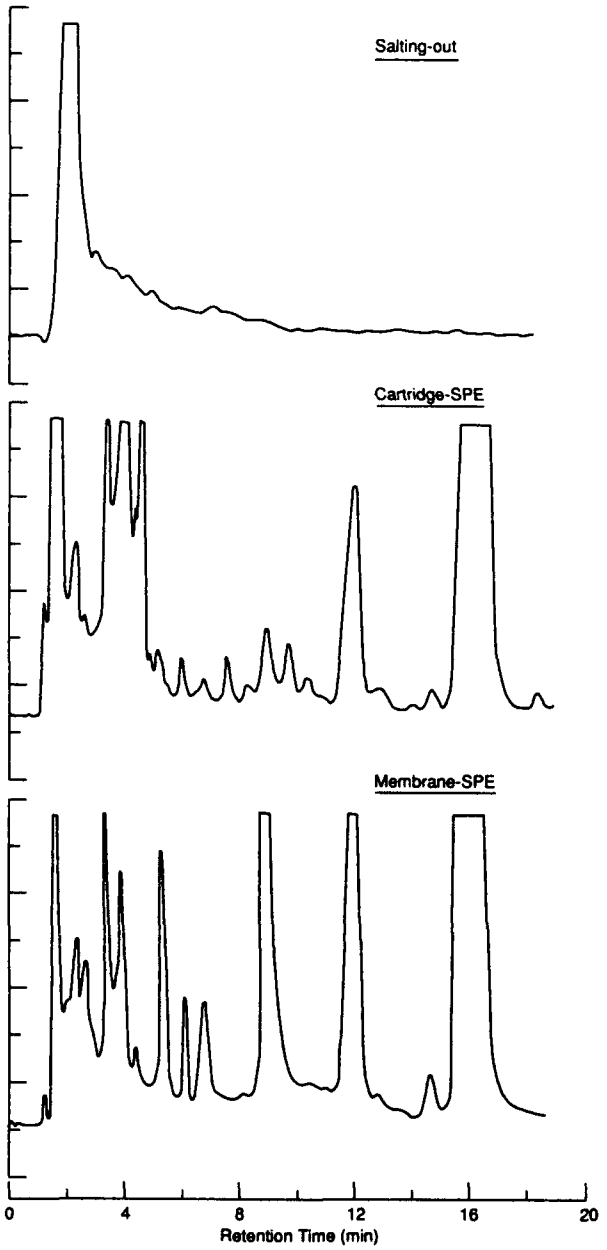

Figure 7. LC-18 chromatograms for sample 20641 from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at WES.

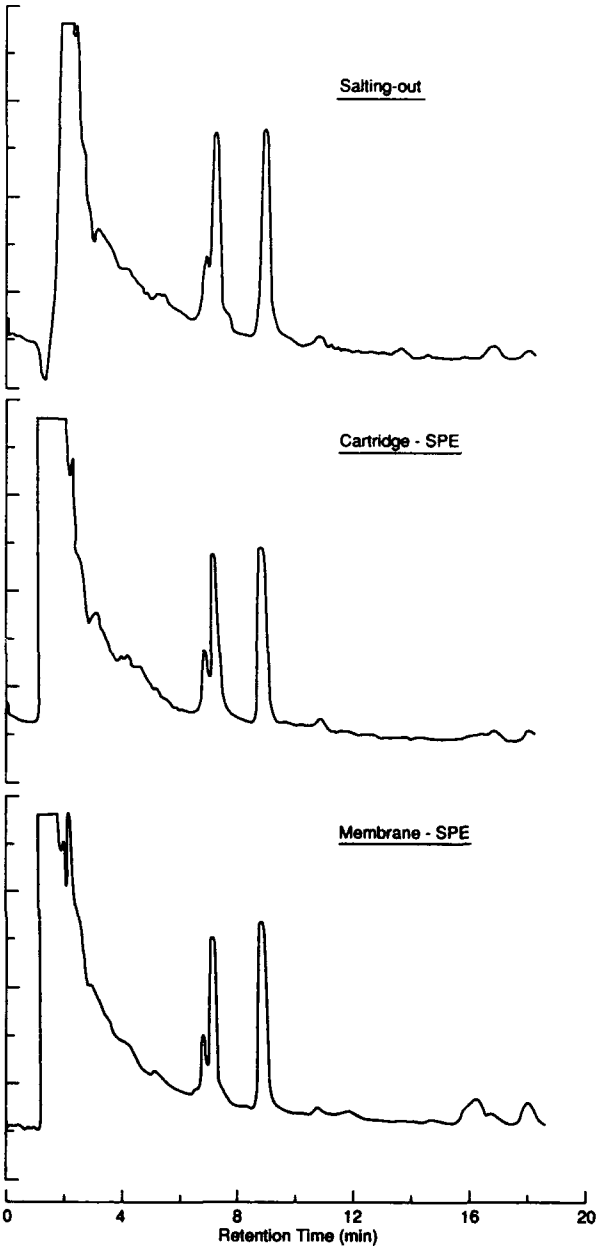

Figure 8. LC-18 chromatograms for sample 20648 from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at WES.

tion methods revealed several different types of situations. Situation 1 was where explosives analytes were present and interferences from the various preconcentration techniques were largely absent. An example of this situation is shown in Figure 5 for sample 20649. Very similarly patterned chromatograms were found for this situation where the absolute peak heights are a function of the initial volume of water used and the final volume of ACN recovered.

For situation 2 the chromatograms for all three methods were blank with respect to explosives analytes and background interferences. An example is shown for sample 20670 (Fig. 6). These chromatograms demonstrate that the solid phase materials used for the membrane-SPE and cartridge-SPE and

the salt and glassware used for the SOE method were clean with respect to UV absorbing interferences.

Situation 3 is demonstrated for sample 20641 (Fig. 7). The chromatogram for the salting-out method is blank with respect to target analytes and interferences, but the chromatograms for both the two solid phase methods, at the same attenuation, show large peaks at a number of retention times across the entire chromatogram. Second column confirmation using a combined LC-8/LC-CN column (Miyares and Jenkins 1991) indicates that none of these peaks result from the presence of nitroaromatic or nitramine explosives. The presence of these peaks, however, would interfere with the ability to detect nitroaromatic and nitramine analytes at concentrations well above the CRLs. These peaks were present for 29 of the 58 groundwater samples from the Rockeye site. In each case, both the cartridge and membrane-SPE samples showed the same patterns of peaks while the salting-out sample was blank. Since the Porapak R and the membranes were cleaned separately and the Porapak R cartridges used for sample 20641 and sample 20670 were packed from material cleaned in the same batch, we do not believe these peaks were a result of poorly cleaned material. Either the samples contained some nonexplosives analytes that were not preconcentrated by the salting-out method, or something present in these samples interacted with the solid phases to either degrade the polymer or release contaminants from within the polymer by swelling the polymer matrix.

Previous experience indicates that salting-out extraction is very efficient at recovering all types of organic analytes (Jenkins and Miyares 1991). Figure 8 shows chromatograms from the three methods obtained on sample 20648 where equivalent preconcentration of nonexplosive compounds was found. For this reason, we do not believe that poor recovery by the SOE procedure is responsible for the lack of these interferences in the SOE extracts. We did note, however, that the volume of acetonitrile recovered in the SOE method, from those samples where this phenomenon was observed, was an average of 1.2 mL greater (5.3 mL vs. 4.1 mL) than for those samples where this phenomenon was not observed. Thus either these samples contained some component that, after salt was added, further reduced the solubility of acetonitrile when compared to other samples, or the samples contained acetonitrile or some other similar solvent.

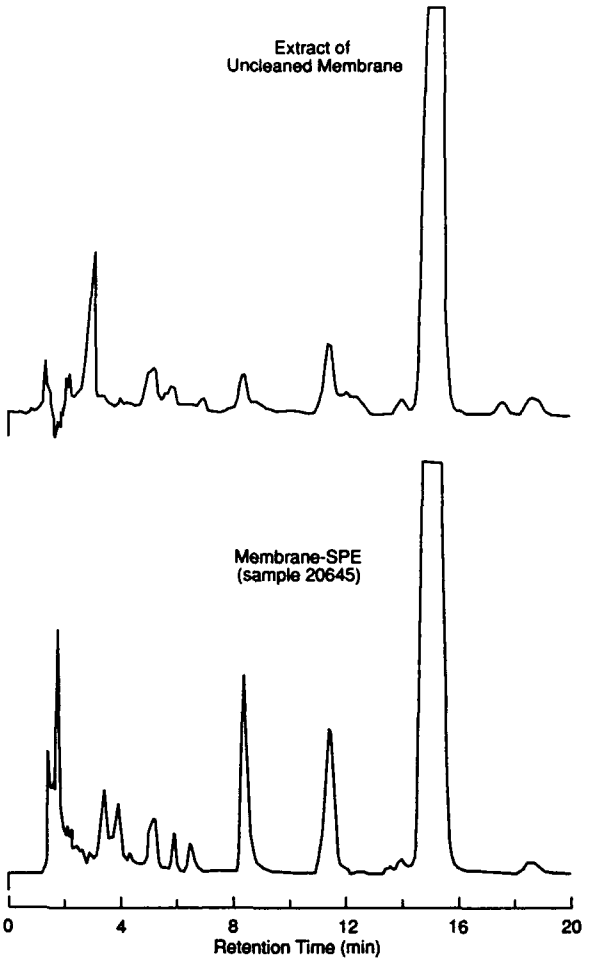

Figure 9. Comparison of LC-18 chromatograms from sample 20645 from Crane-Rockeye Naval Weapons Center preconcentrated by membrane-SPE and the extract from an uncleaned membrane-SPE unit.

To determine if these large peaks in the chromatograms from both SPE methods were originating from the polymers, an uncleaned membrane used for SPE was leached with acetonitrile and analyzed by RP-HPLC. This chromatogram and the chromatogram for the membrane-SPE preconcentrate from sample 20645 are shown in Figure 9. The similar chromatographic patterns suggest that these peaks are coming from the membranes themselves. A similar experiment using uncleaned Porapak R gave identical results (Fig. 10). Thus we conclude that these large peaks are eluting from the solid phases as a result of some component present in a number of these groundwater samples.

To pursue this question, we gathered as much information as we could regarding the composi-

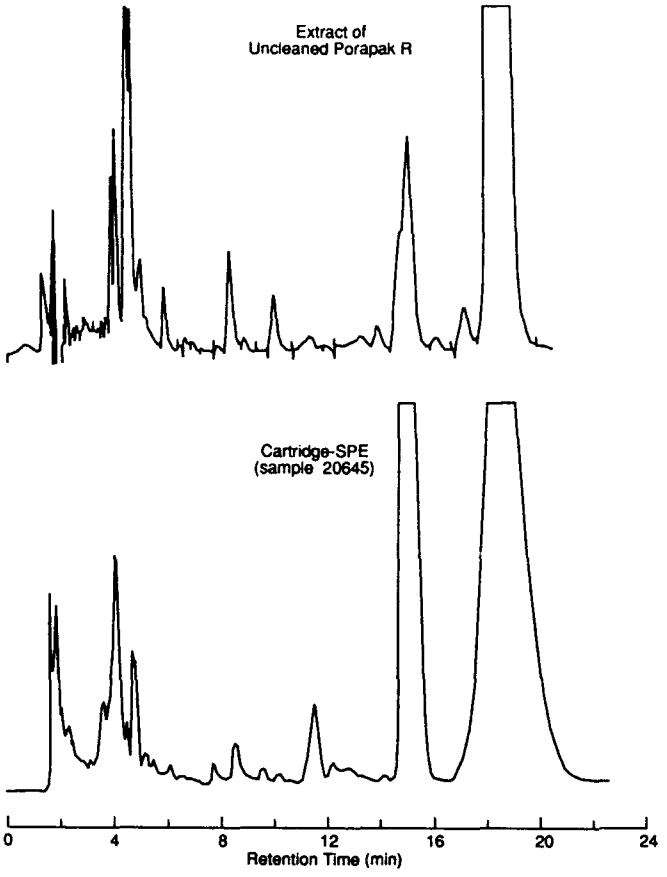

Figure 10. Comparison of LC-18 chromatograms from sample 20645 from Crane-Rockeye Naval Weapons Center preconcentrated by cartridge-SPE and the extract from uncleaned Porapak R.

tion of these groundwaters. Measurements of pH and conductivity for these groundwater samples were obtained during sample collection using a Beckman pH meter (model pHI) and a YSI conductivity meter (model 33M 5-C-T). Inspection of these data indicated that, in general, these samples where these interferences were observed had lower pH and higher specific conductance than those that did not show this problem. The 29 samples demonstrating this problem had pH values ranging from 3.35 to 6.93, with a median value of 5.3. The 29 samples that did not exhibit this problem had pH values ranging from 5.00 to 7.43, with a median value of 6.4. Likewise, median values for specific conductance were 900 and 400 µmhos/cm, respectively, for samples that did or did not demonstrate this problem. Analysis of some of the very acidic samples by ion chromatography yielded SO_4^{-2} levels as high as 2130 mg/L. Initial attempts to duplicate this contamination problem in the laboratory by passing reagent grade water acidified to pH 3.4 with sulfuric acid through an SPE cartridge were unsuccessful.

Second column confirmation

Because the presence of a peak absorbing at 254 nm at the correct retention time is not unequivocal proof of the presence of a target analyte, RP-HPLC procedures for these compounds generally require confirmation on a second RP-HPLC column. For the direct analysis, second column confirmation has been generally conducted using an LC-CN column eluted with 1:1 methanol/water (Jenkins et al. 1989). The elution order for these compounds is very different on the LC-CN column than on the primary analytical column.

Miyares and Jenkins (1991) recommend conducting second column confirmation on extracts from the salting-out procedure using two short columns in series. The reason for the recommended change was that late eluting compounds on the LC-18 column were coeluting interferences on the LC-CN, due to its lower capacity factor for nonexplosives interferences. The short LC-8 column helps to retain these compounds long enough so they no longer interfere when the two columns are used in series. Since information was available on second column confirmation for extracts from the solid phase extraction procedures, we decided to conduct confirmation analysis using the LC-8/LC-CN columns in series.

An example of results obtained for confirmatory analysis is shown in Figure 11. Retention times obtained, however, are somewhat different than reported by Miyares and Jenkins (1991), particularly for HMX (Table 7). We observed HMX eluting at 3.8 minutes instead of 6.9 minutes reported in Table 7.

Nevertheless, the LC-8/LC-CN separation was an effective confirmation separation for samples preconcentrated by the cartridge and membrane-SPE and salting-out methods. In particular, peaks originating from the solid phases, which eluted near the proper retention times for target analytes on the LC-18 column, were shown to be interferences (not confirmed) using the LC-8/LC-CN separation.

Practical considerations

In addition to method performance from a scientific standpoint, the usability of the method from a practical standpoint is also an important issue.

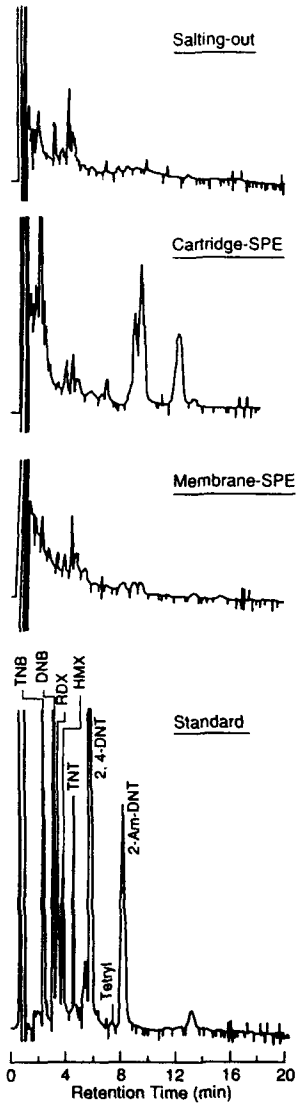

Figure 11. LC-8/LC-CN chromatograms for sample from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE and membrane-SPE methods at WES.

Some important considerations include solvent usage and waste production, labor/processing time requirements, and ruggedness in the hands of the intended users, which are primarily production-oriented, commercial contract laboratories working for the Army. Many times the personnel actually processing samples in these laboratories are nondegree technicians with limited training, while the chemists function in supervisory roles and conduct the actual instrumental analysis. It is important that extraction techniques be as definitive and simplified as possible in order to ensure high quality, reproducible data.

Because of the adverse environmental impact of organic solvents, pressure is mounting to reduce their usage in chemical analysis procedures. In particular, the use of fluorinated and chlorinated organic solvents is being drastically reduced. None of these procedures utilizes any of these solvents during sample processing, although the types and quantities of solvents used in the manufacture and cleaning of the solid phases is unknown to us. All three procedures use acetronitrile to clean the glassware and hardware used in the methods in addition to cleaning and elution of the SPE phases. The salting-out procedure uses a total of 175 mL of ACN per sample for sample processing and approximately 75 mL per sample for glassware preparation, for a total of 250 mL per sample. The cartridge-SPE procedure uses 35 mL of ACN, excluding the 600 mL required for batch extraction of the Porapak R prior to loading the cartridges. Overall usage is estimated at 75 mL per sample. The membrane-SPE method requires only 25 mL of ACN per sample during sample processing. Current cleaning procedures are done individually for each membrane and consume 200 mL per membrane. A more efficient cleaning procedure can probably be developed, but the solvent needs are likely to be at least as great as those for the cartridge-SPE method.

With respect to waste production, a large portion of the ACN obtained from the salting-out procedure will be dissolved in salt water. This could be an advantage or disadvantage depending on how disposal/reuse of this waste is regulated. Cleaning wastes from the SPE materials is contaminated with styrene, divinylbenzene and other polymerization by-products and this may impact disposal options and costs.

Of the three procedures, the membrane-SPE method is the fastest, requiring only 7–10 minutes per sample to extract the analytes from the 500-mL sample. We estimate as many as six samples can be easily processed simultaneously and the procedure does not require flow regulation or careful monitoring. Our experience indicates that a set of 12 samples can be totally processed in about 2 hours. The major operational disadvantages are the current cleaning procedure, requiring soaking of the membrane for several days prior to use and the presence of particulate matter in some samples, which drastically reduces the flow rate through the membrane. This can extend process times, occasionally cause complete blockage and affect analyte recovery as discussed previously.

Use of the cartridge-SPE procedure, particularly with the current design of the extraction manifold, requires considerably more attention to detail than the other methods. First, the flow rate through each cartridge must be maintained at 10 mL/minute or less, which requires constant attention and moni-

toring. We found that processing of more than six cartridges at a time led to confusion and the possibility of sample spillage or cross contamination. Total processing time for 12 samples is estimated at 3.5 to 4 hours. Like the membrane, particulate matter in samples reduced flow rates through the cartridge, thereby extending sample processing time. Of the three procedures, we judge this method to be the most demanding with regard to attention to detail and thus the least rugged in day-to-day usage.

Experience with the salting-out procedure indicated that as many as 12 samples could be easily processed simultaneously. We estimate a batch of 12 samples could be processed in about 3.5 to 4 hours. Once stirring of the samples is initiated, they can be left unattended for 15-minute increments. Little attention to detail is needed except during liquid transfer steps. The major disadvantages to this procedure is the need to measure the volume of each extract, which differs by a greater amount than do the volumes of extracts from the other two methods, and the need to avoid transferring drops of NaCl saturated water during the final step.

CONCLUSIONS AND RECOMMENDATIONS

SOE and cartridge- and membrane-SPE were compared with respect to their ability to preconcentrate nitroaromatic and nitramine explosives from water prior to RP-HPLC analysis. Both fortified reagent grade water and contaminated groundwater samples were used in this assessment.

Low detection capability and overall precision were comparable among the three procedures. Recoveries of HMX and RDX are better using cartridge-SPE and SOE than membrane-SPE. The actual percent recovery of these two analytes seem to be sample specific for the membrane procedure. Recovery of the nitroaromatics was acceptable for all three procedures.

At present the major problems associated with the use of the SPE procedures are the inadequacy of the current cleaning procedures. While use of the Soxhlet procedure on a batch basis for the Porapak R material appears to be adequate, cleaning must be accomplished just before use or the contamination reappears, apparently by diffusion from the interior of the polymer. The cleaning procedure we used for the membranes (sequential soaking for each membrane) is cumbersome and solvent wasteful.

Problems with interferences were encountered using both the cartridge-SPE and membrane-SPE procedures for a number of actual ground water samples. These interferences appeared to be identical to the compounds released from the solid phases during cleaning, but were apparently released from the SPE phases due to a matrix interaction with a number of ground water samples. The nature of this interaction is still unclear. These compounds would interfere with determination of nitroaromatic and nitramine explosives even at reasonably high concentrations.

All three procedures were evaluated with respect to usability under a production laboratory scenario. The membrane-SPE procedure is the easiest and the fastest. The cartridge-SPE and SOE procedures appeared to be about equal in time requirement to process a batch of 12 samples, although with some equipment improvements the cartridge procedure could be made somewhat more efficient. We are concerned, however, about the potential for cross contamination that exists using the cartridge procedure with the currently available manifold design.

The elimination of the need to use evaporative preconcentration with the salting-out procedure is a major improvement. We believe the new procedure will be more precise and less subject to error in routine use than the initial method which utilized a Kudena–Danish evaporator.

Second column confirmation was used on sample extracts from groundwater samples for all three methods. Current confirmation separations, however, appeared to be inadequate for some analytes in extracts preconcentrated by the various methods tested. We recommend additional development of separation technology for confirmation of target analytes.

The observation of interferences apparently released from the SPE phases during sample extraction of groundwater samples is an important finding. In the past, interferences released from these SPE polymers have been attributed to differences in the cleanliness of these materials from batch to batch. Inconsistent cleaning does not appear to be the cause of the interferences we observed here. Rather the release of interferences is a result of matrix interactions.

In summary, the SOE, cartridge-SPE and membrane-SPE preconcentration techniques are all capable of providing adequate analyte preconcentration of nitroaromatics and nitramines prior to RP-HPLC determination. Of the three, the SOE method appears to be the least prone to interfer-

ences. The membrane-SPE method requires the least sample processing time, but its recovery of HMX is the poorest of the three methods. The cartridge-SPE method requires the least solvent per sample, but its routine use with the currently available processing manifold appears prone to problems with cross contamination.

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APPENDIX A: RESULTS OF 4-DAY USATHAMA CERTIFICATION TEST

Table A1. Results of 4-day USATHAMA certification test, HMX, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0	0	0	0	0	0
0.5X	0.6	0.21	0.22	0.17	0.20
X	0.11	0.30	0.28	0.21	0.28
2X	0.23	0.40	0.39	0.29	0.40
5X	0.57	0.77	0.75	0.68	0.74
10X	1.14	1.29	1.31	1.23	1.33

Table A2. Results of 4-day USATHAMA certification test, RDX, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0.39	0.47	0.48	0.51
0.5	0.05	0.44	0.39	0.38	0.61
X	0.10	0.59	0.47	0.42	0.46
2X	0.21	0.63	0.54	0.55	0.49
5X	0.52	1.02	0.92	0.98	0.90
10X	1.04	1.76	1.57	1.65	1.50

Table A3. Results of 4-day USATHAMA certification test, TNB, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5	0.04	0.06	0.08	0.07	0.05
X	0.08	0.14	0.11	0.12	0.11
2X	0.17	0.19	0.21	0.21	0.23
5X	0.41	0.53	0.53	0.57	0.56
10X	0.82	1.06	1.06	1.12	1.16

Table A4. Results of 4-day USATHAMA certification test, DNB, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5	0.05	0.07	0.06	0.07	0.07
X	0.10	0.16	0.13	0.13	0.13
2X	0.21	0.24	0.25	0.23	0.25
5X	0.52	0.61	0.60	0.62	0.61
10X	1.04	1.20	1.20	1.20	1.22

Table A5. Results of 4-day USATHAMA certification test, tetryl, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5	0.05	0.06	0.08	0.08	0.08
X	0.09	0.12	0.11	0.13	0.10
2X	0.19	0.13	0.22	0.25	0.28
5X	0.46	0.27	0.35	0.39	0.45
10X	0.93	0.55	0.71	0.88	1.09

Table A6. Results of 4-day USATHAMA certification test, TNT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5	0.05	0.11	0.10	0.09	0.11
X	0.10	0.18	0.16	0.16	0.16
2X	0.20	0.28	0.26	0.25	0.26
5X	0.49	0.57	0.61	0.59	0.61
10X	0.98	1.09	1.14	1.13	1.22

Table A7. Results of 4-day USATHAMA certification test, 1-Am-DNT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.09	0.08	0.07	0.07
X	0.10	0.14	0.14	0.13	0.15
2X	0.21	0.24	0.25	0.21	0.25
5X	0.52	0.59	0.61	0.62	0.64
10X	1.04	1.17	1.20	1.19	1.21

Table A8. Results of 4-day USATHAMA certification test, 2,4-DNT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.09	0.06	0.07	0.08
X	0.10	0.12	0.12	0.15	0.14
2X	0.20	0.25	0.34	0.22	0.25
5X	0.50	0.57	0.57	0.58	0.59
10X	1.01	1.10	1.11	1.11	1.11

Table A9. Results of 4-day USATHAMA certification test, o-NT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0	0	0.08	0.08
X	0.11	0.13	0.15	0.17	0.13
2X	0.21	0.25	0.26	0.24	0.24
5X	0.54	0.56	0.63	0.64	0.57
10X	1.07	1.15	1.16	1.18	1.11

Table A10. Results of 4-day USATHAMA certification test, p-NT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0	0	0	0.07
X	0.11	0.15	0.16	0.18	0.14
2X	0.21	0.23	0.27	0.20	0.23
5X	0.53	0.55	0.60	0.57	0.55
10X	1.06	1.09	1.13	1.10	1.08

Table A11. Results of 4-day USATHAMA certification test, m-NT, by cartridge-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.06	0.09	0	0	0.11
X	0.12	0.18	0.13	0.21	0.17
2X	0.25	0.29	0.26	0.27	0.28
5X	0.62	0.64	0.64	0.66	0.67
10X	1.23	1.26	1.23	1.26	1.21

Table A12. Results of 4-day USATHAMA certification test, HMX, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.06	0.19	0.19	0.13	0.22
X	0.11	0.24	0.25	0.16	0.26
2X	0.23	0.39	0.40	0.30	0.38
5X	0.57	0.74	0.69	0.65	0.69
10X	1.14	1.25	1.30	1.21	1.33

Table A13. Results of 4-day USATHAMA certification test, RMX, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0.11
0.5X	0.05	0.12	0.13	0.14	0.08
X	0.10	0.15	0.17	0.17	0.11
2X	0.21	0.25	0.27	0.32	0.23
5X	0.52	0.56	0.63	0.62	0.60
10X	1.04	1.14	1.19	1.14	1.09

Table A14. Results of 4-day USATHAMA certification test, TNB, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.04	0.09	0.05	0.10	0.06
X	0.08	0.12	0.13	0.12	0.12
2X	0.17	0.24	0.21	0.24	0.21
5X	0.41	0.51	0.50	0.52	0.55
10X	0.82	1.02	0.99	0.95	1.03

Table A15. Results of 4-day USATHAMA certification test, DNB, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.08	0.06	0.10	0.06
X	0.10	0.12	0.03	0.11	0.12
2X	0.21	0.24	0.23	0.23	0.23
5X	0.52	0.55	0.55	0.54	0.55
10X	1.04	1.09	1.05	1.03	1.09

Table A16. Results of 4-day USATHAMA certification test, tetryl, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.07	0.08	0.24	0.07
X	0.09	0.13	0.12	0.13	0.12
2X	0.19	0.24	0.23	0.29	0.24
5X	0.46	0.44	0.39	0.54	0.53
10X	0.93	0.78	1.01	0.88	0.93

Table A17. Results of 4-day USATHAMA certification test, TNT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.07	0.07	0.16	0.08
X	0.10	0.13	0.09	0.12	0.15
2X	0.20	0.22	0.23	0.24	0.23
5X	0.49	0.53	0.55	0.56	0.55
10X	0.98	1.02	1.06	1.01	1.08

Table A18. Results of 4-day USATHAMA certification test, 2-Am-DNT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.06	0.07	0.18	0.08
X	0.10	0.14	0.17	0.11	0.15
2X	0.21	0.23	0.24	0.23	0.25
5X	0.52	0.59	0.58	0.56	0.57
10X	1.04	1.09	1.06	1.01	1.12

Table A19. Results of 4-day USATHAMA certification test, 2,4-DNT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.06	0.08	0.14	0.08
X	0.10	0.11	0.06	0.11	0.13
2X	0.20	0.22	0.23	0.22	0.22
5X	0.50	0.54	0.54	0.54	0.54
10X	1.04	1.02	1.03	1.01	1.05

Table A20. Results of 4-day USATHAMA certification test, o-NT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.08	0.09	0.24	0.11
X	0.11	0.12	0.12	0.13	0.15
2X	0.21	0.25	0.24	0.24	0.25
5X	0.54	0.59	0.58	0.61	0.57
10X	1.07	1.14	1.11	1.12	1.10

Table A21. Results of 4-day USATHAMA certification test, p-NT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.10	0.11	0.31	0.15
X	0.11	0.16	0.19	0.11	0.20
2X	0.21	0.26	0.22	0.19	0.30
5X	0.53	0.61	0.58	0.54	0.64
10X	1.06	1.06	1.06	1.19	1.25

Table A22. Results of 4-day USATHAMA certification test, m-NT, by SOE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.06	0.10	0.11	0.26	0.15
X	0.12	0.16	0	0.17	0.20
2X	0.25	0.21	0.28	0.29	0.30
5X	0.62	0.68	0.64	0.66	0.64
10X	1.23	1.22	1.22	1.19	1.25

Table A23. Results of 4-day USATHAMA certification test, HMX, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.06	0.23	0.20	0	0.22
X	0.11	0.26	0.27	0.21	0.28
2X	0.23	0.34	0.35	0.24	0.36
5X	0.57	0.57	0.60	0.56	0.62
10X	1.14	1.03	0.98	0.97	0.99

Table A24. Results of 4-day USATHAMA certification test, RDX, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0.09	0.09	0.10	0
0.5X	0.05	0.09	0.14	0.15	0
X	0.10	0.14	0.23	0.21	0.18
2X	0.21	0.31	0.31	0.28	0.31
5X	0.52	0.64	0.67	0.70	0.60
10X	1.04	1.26	1.24	1.28	1.28

Table A25. Results of 4-day USATHAMA certification test, TNB, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.04	0.07	0.08	0.06	0.07
X	0.08	0.07	0.13	0.11	0.12
2X	0.17	0.19	0.21	0.23	0.21
5X	0.41	0.51	0.48	0.55	0.50
10X	0.82	0.90	0.94	1.00	1.02

Table A26. Results of 4-day USATHAMA certification test, DNB, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0 X	0	0	0	0	0
0.5X	0.05	0.06	0.07	0.06	0.06
X	0.10	0.11	0.14	0.11	0.13
2X	0.21	0.22	0.23	0.25	0.22
5X	0.52	0.59	0.52	0.56	0.56
10X	1.04	1.14	1.05	1.09	1.05

Table A27. Results of 4-day USATHAMA certification test, tetryl, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.05	0.07	0.07	0.05
X	0.09	0.06	0.14	0.09	0.12
2X	0.19	0.08	0.20	0.21	0.23
5X	0.46	0.24	0.69	0.56	0.41
10X	0.93	0.34	0.82	0.91	0.98

Table A28. Results of 4-day USATHAMA certification test, TNT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.07	0.11	0.10	0.05
X	0.10	0.12	0.15	0.16	0.12
2X	0.20	0.22	0.24	0.28	0.23
5X	0.49	0.51	0.42	0.56	0.41
10X	0.98	1.00	0.98	1.01	0.98

Table A29. Results of 4-day USATHAMA certification test, 2-Am-DNT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.08	0.08	0.07	0.04
X	0.10	0.11	0.12	0.14	0.11
2X	0.21	0.22	0.21	0.26	0.22
5X	0.52	0.56	0.66	0.57	0.55
10X	1.04	1.13	1.03	1.09	1.04

Table A30. Results of 4-day USATHAMA certification test, 2,4 DNT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.06	0.07	0.07	0.08
X	0.10	0.10	0.11	0.10	0.10
2X	0.20	0.19	0.19	0.21	0.19
5X	0.50	0.49	0.46	0.51	0.48
10X	1.01	1.01	0.91	0.97	0.91

Table A31. Results of 4-day USATHAMA certification test, 0-NT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0.15	0	0.10	0.16
X	0.11	0.10	0.17	0.17	0.16
2X	0.21	0.25	0.20	0.32	0.21
5X	0.54	0.57	0.46	0.60	0.51
10X	1.07	1.11	1.00	1.04	0.93

Table A32. Results of 4-day USATHAMA certification test, p-NT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.05	0	0.11	0	0.18
X	0.11	0.12	0.16	0	1.38*
2X	0.21	0.13	0.18	0.22	0.17
5X	0.53	0.52	0.39	0.49	0.51
10X	1.06	1.05	0.92	0.99	0.85

* This outlier removed and replaced by a value of 0.09.

Table A33. Results of 4-day USATHAMA certification test, m-NT, by membrane-SPE.

Target concentration		*Found concentration (µg/L)*			
Level	*µg/L*	*Day 1*	*Day 2*	*Day 3*	*Day 4*
0X	0	0	0	0	0
0.5X	0.06	0.27	0.13	0.14	0.21
X	0.12	0.25	0.21	0.16	0.26
2X	0.25	0.27	0.28	0.25	0.25
5X	0.62	0.67	0.37	0.60	0.58
10X	1.23	1.25	1.07	1.13	1.06

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13. ABSTRACT (*Maximum 200 words*)

Salting-out solvent extraction (SOE) was compared with cartridge and membrane solid phase extraction (SPE) for preconcentration of nitroaromatic and nitramine explosives from water, prior to reversed-phase high performance liquid chromatographic analysis (RP-HPLC). The procedures were compared initially using reagent grade water fortified with TNT, RDX, HMX and nine other analytes at concentrations below what could be determined without preconcentration and the results were used to estimate analyte recovery and the low concentration detection capability, as characterized by the Certified Reporting Limit (CRL). CRLs for the three procedures were comparable with values generally in the range of 0.05 to 0.30 µg/L. Percentage recoveries for the three procedures were generally greater than 90%, except for those of HMX and RDX obtained by the membrane-SPE procedure. A second comparison among the three procedures was obtained on 58 groundwater samples from the Rockeye site at the Naval Surface Warfare Center, Crane, Indiana. Results from a direct analysis procedure were compared to those from the three preconcentration techniques to estimate percent recovery of HMX, RDX and TNT for real samples. Recoveries were greater than 80% except for HMX and RDX by the membrane-SPE method. Both SPE procedures exhibited background interferences, which the authors attribute to matrix interaction with the SPE polymers. Usability of the three procedures in a production-oriented laboratory was evaluated with emphasis on solvent consumption, waste production and sample processing time. The cartridge-SPE was judged to be the least rugged of the three procedures.

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